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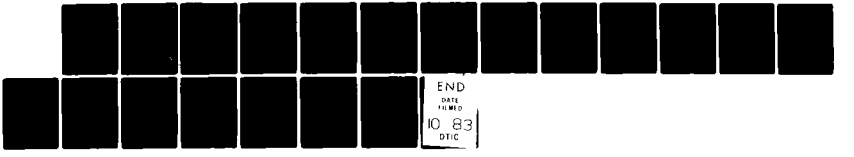

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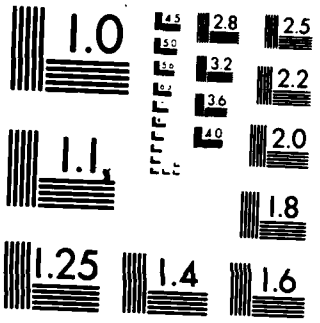

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DEVELOPMENT OF ANALYTICAL METHODOLOGY FOR THE MEASUREMENT OF CHLORINE AND BROMINE IN THE STRATOSPHERE

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Suitable methodology based on neutron activation analysis is developed for accurate measurement of chlorine and bromine from balloon flight sampling. The method is applied to measurement of a number of filter and filter extracts. It is shown that analyses carried out on total filter is inaccurate because of the relatively major filter blank contributions. However, analyses carried out on water extracts of filters appear to yield satisfactory measurements.

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SUMMARY

This final report summarizes the work carried out during the period 20 November 1980 to 20 November 1982. The work concerns development of a Radiochemical Procedure based on Neutron Activation Analysis for simultaneous measurements of chlorine and bromine on filter membranes and their appropriate aqueous extracts.

The work reported here consists of two phases:

1. Development of measurement procedures.
2. Measurements carried out on returned filter membranes and their aqueous extracts.

The analytical developments carried out in this work support the following conclusions: a) chlorine can be measured directly without the need for radiochemical separations, b) both chlorine and bromine can be measured simultaneously employing a postirradiation chemical separation with $AgNO_3$, c) at appropriate levels of analyses, the measurements can be carried out with analytical precisions (relative standard deviation) of about 10%, and d) the filter contamination levels, although obviously dependent on the filter membrane employed, are often too high to allow direct measurements so that satisfactory methods are necessary to separate the sample halogen from filter membrane prior to measurement.

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1. INTRODUCTION

Accurate measurement of halogens from stratospheric sample collections requires development of a sensitive method, preferably capable of simultaneous measurements. Neutron activation analysis can potentially provide this tool (1). All four members of the halogen group yield radioisotopic products with suitable gamma photon emissions upon irradiation with thermal neutrons from a medium-flux nuclear reactor (2). The characteristics of the nuclear reactions involved and quantitative data on critical parameters of these reactions are given in Table 1 and indicate that except for fluorine, the method possesses the potential sensitivity required for accurate measurements at suitable analyte levels.

This final report is concerned with the development, and subsequent application, of neutron activation analysis to measurement of chlorine and bromine, with special reference to the former element in stratospheric samples returned from balloon flights. The balloon flights were conducted by the Air Force Geophysics Laboratory using their launch facility at Holloman Air Force Base, New Mexico (33°N). The filters were mounted in a direct flow sampler which utilizes a Torrington blower to pull air at high velocities through the filter paper.

TABLE 1.1

RELEVANT FUNDAMENTAL PARAMETERS FOR NEUTRON

ACTIVATION OF HALOGENS WITH THERMAL NEUTRONS (2)

Element	Nuclear Reaction	Half Life of Produced Isotope	Gamma Photons (MeV)	Reaction Cross Section (b)
F	$^{19}F\ (n,\gamma)\ ^{20}F$	11 s	1.63	.010
Cl	$^{37}Cl\ (n,\gamma)\ ^{38}Cl$	37 m	1.60	.40
Br	$^{79}Br\ (n,\gamma)\ ^{80}Br$	18 m	.618	8.5
	$^{81}Br\ (n,\gamma)\ ^{82}Br$	35 h	.777	3
I	$^{127}I\ (n,\gamma)\ ^{128}I$	25 m	.441	6.4

2. EXPERIMENTAL

The experiments carried out for this work fall into two categories: 1) development and evaluation of the analytical method, and 2) limited measurements on returned samples. All irradiations were carried out in the pneumatic facility (1PH1) of the MIT-RR whose thermal neutron flux is at the nominal value of 5×10^{12} n cm^{-2} s^{-1}, and whose neutron activation parameters are fully described elsewhere (3).

2.1 Methods Development

A number of neutron activation studies were carried out to evaluate such fundamental system characteristics as measurement precision, background contributions, filter contamination levels, etc. for intrumental measurement of chlorine. Following these, a radiochemical procedure was developed and tested to measure simultaneously both chlorine and bromine. The instrumentation employed was based on high-resolution gamma spectrometry, whose characteristics have been described previously (3) (Canberra Industries Multichannel Analysis System 8180; detector resolution 2.0 kev; efficiency 15% nominal).

The radiochemical procedure developed for filter leachates was as follows:

1. Sample irradiated for 5 minutes.
2. Transfer sample to 250 ml beaker quantitatively.
3. Heat solution on hot plate.
4. Add 1 ml 0.6 mmolar solution of $AgNO_3$ and carrier solution containing 1.8 mg chloride and 1.5 mg bromide ions.

5. Bring to boil; let cool.

6. Filter precipitate of $Ag^{38}Cl$ and $Ag^{80}Br$.

7. Count for ^{38}Cl and ^{80}Br activity.

The above procedure was tested against chlorine measurements carried out instrumentally to establish the accuracy.

2.2 Measurements of Filters and Leachates

A number of measurements were carried out on filter blanks, filters returned from flights and filter leachates. The sample processing prior to receipt at MIT was carried out by other laboratories and this report is concerned only with the portion of the work carried out at MIT. The filter membranes employed in the analytical methodology development phase of the work are obtained from Millipore Corp., Bedford, MA, and are of the type Fluoropore. Those employed in balloon sampling are IPC-1478, and are further described in the footnote of Table 3.3 (also ref. 4).

3. RESULTS AND DISCUSSION

3.1 Methods Development

Results related to methods development are summarized in Tables 3.1 and 3.4. Data given in Table 3.1 illustrate the analytical measurement precision (reproducibility) of the method. It is clear that relative standard deviations for both chlorine and sodium spiked on filter membranes are better than 10% at the spiked levels of 6.3 μg for chlorine and 4.1 μg for sodium. However, it is equally clear that the background levels, especially for chlorine, of the filter membrane may vary significantly, potentially resulting in serious error if the analyte level approaches that present in the filter membrane. This is a serious shortcoming for the filter membranes employed in actual in-flight sampling as will be discussed below.

The comparison between the instrumental and radiochemical methods for the measurement of chlorine was made by analysis of four aqueous extracts as summarized in Table 3.4. The results indicate satisfactory comparison between the two methods and imply quantitative recovery of ^{38}Cl from the radiochemical procedure.

3.2 Filter Blank Levels

The chlorine level of blank filters and filter parts provided by Dr. Bruce Gandrud of the National Center for Atmospheric Research (Boulder, CO) was measured in order to establish the suitability of these materials. The data are summarized in Table 3.2. It is evident that total filters of the type analyzed contain a very significant amount of chlorine. The major portion of the chlorine is resident within the filter material, but chlorine

content of the support is also significant. Treatment with TBAH reduced chlorine content significantly, but the treated material still contains about 2 μg chlorine for the support and significantly larger amounts in the membrane itself. These analyses indicate that total chloride measurements carried out without extracting the sample are not likely to provide a suitable method for measurement of submicrogram quantities expected.

3.3 Chlorine and Bromine Measurements on Flight Samples

Four samples - designated as Hi S, Hi C; Lo S, and Lo C (Dr. Bruce Gandrud, NCAR) - were analyzed for total chlorine. The results are summarized in Table 3.3. The results show again the large and variable content of chlorine which is most likely due to chlorine contamination of the filter itself. The analyses of water extracts of these filters (extraction carried out at NCAR) were compared with measurements made at NCAR using the method described previously (4), and the comparative data are given in Table 3.5. The agreement between the two laboratories appears to be very good. Comparing the extracts from samples (Hi S and Lo S) with their corresponding controls, respectively, shows the enhanced level of chlorine in the sample extracts.

Finally a number of water extracts (submitted by Los Alamos National Laboratory) were analyzed for both chlorine and bromine and the results of these analyses are summarized in Table 3.6.

As noted in Tables 3.5 and 3.6, the reported analyses are for balloon flights conducted in 1981 (Table 3.5), and 1982 (Table 3.6) for which sample extractions were carried out at NCAR (Table 3.5) or Los Alamos National Laboratory (Table 3.6), respectively, and chlorine and bromine analyses were done at MIT (and NCAR for Table 3.5).

TABLE 3.1

DETERMINATION OF SENSITIVITY AND REPRODUCIBILITY

OF Cl MEASUREMENTS*

Sample No.	Treatment	Peak Areas** ^{38}Cl, 2166 kev	Peak Areas** ^{24}Na, 2754 kev
1	Filter blank	2968	491
2	" "	3980	474
3	" "	1193	510
4	Fil. bl. + 10.4 µg NaCl	46835	20447
5	" " "	49620	21261
6	" " "	44046	19963
	Average for Samples 4-6 ± 1 SD	46833 ± 2787	20559 ± 655

* Filter membranes are Fluoropore filters (Millipore Corp., Bedford, MA). Irradiation conditions: $\phi_{th} = 5 \times 10^{12}$ ncm^{-2}s^{-1}; facility = 1 pH1; t_1 = 10 min.; t_d = 6 - 47 min.; t_c = 1000 sec.

** Corrected to EOB (End of Bombardment).

TABLE 3.2

SUMMARY OF Cl MEASUREMENTS ON FILTER MEMBRANES FROM NCAR

Sample ID	µg Cl/sample
IPC-1; filter	76.4
IPC-2; filter	79.4
IPC-3; filter	78.8
IPC-1; support	12.9
IPC-2; support	6.9
IPC-3; support	7.1
Plastic Bag-1	1.3
Plastic Bag-2	4.9
Plastic Bag-3	N.D.
1 ml. MeOH-1	N.D.
1 ml. MeOH-2	N.D.
TBAH-treated-filter	17.
TBAH-treated-support-1	2.4
TBAH-treated-support-2	2.1

TABLE 3.3

TOTAL CHLORINE ANALYSES OF FILTER PORTIONS AS RECEIVED

(1981 BALLOON FLIGHTS)

Sample Designation*	Chlorine Content, µg/sample
Lo S	111.
Lo C	182.
Hi S	96.
Hi C	92.

*Filters are IPC-1478, a low pressure drop cellulose filter. The filters are purified and impregnated with an inert organic oil, dibutoxyethylphthallate, to improve the collection efficiency for particulate species. The filter portions designed to also gather acidic species are treated with tetrabutyl ammonium hydroxide (TBAH), a strong organic base (4).

Lo S - Filter exposed at 20 km on 31 May 1981

Lo C - Blank portion of filter

Hi S - Filter exposed at 30-25 km on 4 June 1981

Hi C - Blank portion of filter

TABLE 3.4

COMPARISON BETWEEN THE INSTRUMENTAL AND RADIOCHEMICAL METHODS FOR THE MEASUREMENT OF CHLORINE IN FILTER EXTRACTS*

(1981 BALLOON FLIGHTS)

Sample ID	µg Chlorine Found/ml Solution		µg Br/ml
	Instrumental Method	Radiochemical Method	
HS	2.33	2.18	.035
HC	1.43	1.24	.015
LS	3.61	4.12	.064
LC	1.49	1.44	.023

* Filters are IPC-1478; see footnote of Table 3.3 for further details. For exposure conditions see footnote of Table 3.3.

TABLE 3.5

TOTAL CHLORINE ANALYSES OF WATER EXTRACTS

(1981 BALLOON FLIGHTS)

Sample ID*	MIT Analyses, µg Cl/ml	NCAR, µg CL/ml
Hi S	2.33	2.39
Hi C	1.43	1.46
Lo S	3.61	3.74
Lo C	1.49	1.57

*See footnote of Table 3.3 for description of filters and exposure conditions.

TABLE 3.6

SUMMARY OF ANALYSES ON WATER EXTRACTS FROM LOS ALAMOS NATIONAL LABORATORY (UNITS: μg/ml)

(April 6, 1982 BALLOON FLIGHT)

Sample ID*	Br	Cl
BL-BB	.029	2.6
Lo-BB	.033	2.8
HI-BB	.027	2.7
BL-BS	.028	2.5
Lo-BS	.060	3.4
HI-BS	.088	4.9
BL-NB	.0081	.48
Lo-NB	.012	.46
HI-NB	.024	.56
BL-NS	.0077	.82
Lo-NS	.014	.68
HI-NS	.014	.89

*BL - Blank Filter
Lo - Filter exposed at 15 km
HI - Filter exposed at 20 km
NB - Neutral blank portion (1/6) of filter
BB - Basic (TBAH impregnated) blank portion (1/6) of filter
NS - Neutral sample portion (1/3) of filter
BS - Basic sample portion (1/3) of filter

The NB and BB portions were extracted in 25.0 ml H_2O while the NS and BS portions were extracted in 50.0 ml H_2O.

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